



Catalytic HDC/HDN of 4-chloronitrobenzene in water under ambient-like conditions with Pd supported on pillared clay

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ABSTRACT

Hydrotreatment of 4-chloronitrobenzene in aqueous phase has been carried out under ambient-like operating conditions (25 °C and 1 atm) with H₂ using an own-prepared catalyst based on Pd (1 wt%) supported on Al-pillared clay. Nitrobenzene, 4-chloroaniline, aniline and cyclohexanone were identified as reaction byproducts and trace amounts of different azobenzenes were also detected. Complete dechlorination was achieved in around 1.5 h reaction time. Experiments with the aforementioned nitrogenated byproducts were performed to elucidate the reaction pathway. Nitrobenzene was completely converted in short reaction time leading to aniline as main product. Disappearance of 4-chloroaniline was complete after 1 h giving rise to aniline as primary product. An unstable imine/enamine was obtained from aniline, yielding cyclohexanone upon reaction with water. Hydrodenitrogenation of aniline was favored at acidic pH, being released more than 85% N after 10 h. A kinetic analysis is included and values of activation energy are given.

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1. Introduction

Chloronitrogenated aromatic compounds such as chloroanilines and chloronitrobenzenes are usually classified as toxic agents [1] that can cause cancer [2] and other harmful effects. Nevertheless these molecules are widely used in the production of pesticides, antioxidants, dyes and other chemicals. Chloroanilines are forbidden in many countries [3] and the European Union restricts the use of some azo-dyes in the textile industry because of the potential formation of that kind of compounds (EU Directive 2002/61/CE). 4-chloroaniline (4-CA) is used in the manufacture of some pesticides approved by the EU such as pyraclostrobin and diflubenzuron, as well as different drugs, dyes and biocides widely used in healthcare products, such as chlorhexidine or triclocarban. On the other hand, 4-chloronitrobenzene (4-CNB) is used in the manufacture of 4-CA. Aniline is used in the synthesis of different organic compounds, like methylene diphenyl diisocyanate (MDI) antioxidants, pesticides and dyes among others. The presence of those species in industrial wastewaters causes serious problems requiring the development of cost-effective solutions. Catalytic HDC/HDN appears as an emerging technology capable of working at mild conditions leading to

low-toxicity biodegradable byproducts upon hydrodechlorination (HDC) and hydrodenitrogenation (HDN).

HDC has been investigated in the last decade with the aim of reducing the toxicity associated to chlorinated water pollutants like chlorophenols [4–7]. However, little has been reported so far on the hydrotreatment of chloronitrogenated compounds in water. Some work has been done with 4-chloronitrobenzene [8–11] and 4-chloroaniline [12,13]. The works on the HDC of chloronitrobenzenes and chloroanilines represent a little percentage of the ones carried out in liquid phase [14].

Different processes for the hydrogenation and HDN of aniline in aqueous and non-aqueous media have been described in the literature [15–21]. All these works use severe operating conditions. Different products of aniline HDN have been reported depending on the operation conditions and the catalysts used: cyclohexylamine, benzene, cyclohexane, cyclohexene, cyclohexanol, cyclohexanone and different condensation products as dicyclohexylamine, N-phenylcyclohexylamine or diphenylamine and ammonia [21].

Some catalytic and non catalytic methods have been reported for the cleavage of the C–N bond [22]. HDN in aqueous phase can take place at low temperature and atmospheric pressure upon hydrolysis of the labile imines resulting from hydrogenation. HDN of aniline leads to carbonyl compounds as ketones. The denitrogenation of some amines, like aniline, in aqueous phase at low pressure and temperature (22.5 °C) has been studied using Pd/BaSO₄ as catalyst

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[23,24]. Catalysts based in precious metals like Pd or Rh, promote the cleavage of the C–N bond of amines using H₂ as reducing agent and H₂O as reagent allowing nucleophilic substitution of N by O, referred as “reductive hydrolysis” [25].

Catalytic HDC/HDN of 4-CNB can have some important advantages compared to other potential solutions, like catalytic oxidation or biological treatments. The most important is the possibility of achieving complete dechlorination so that highly toxic chlorinated intermediates are not remaining. The good stability of the catalyst is also an important issue. Catalytic oxidation leads to the generation of a great diversity of highly toxic intermediates, including chlorinated species [26] in addition to the azobenzenes produced from aniline oxidation [27]. On the other hand biological treatments are limited by the high toxicity and poor biodegradability of 4-CNB and its intermediates [28,29].

The aim of this paper is to study HDC and HDN of 4-CNB in aqueous phase under ambient-like operating conditions using a own-prepared catalyst based on Pd supported on pillared clay, which has shown a fairly high activity in the HDC of chlorophenols in previous works [30]. The reaction pathway has been investigated from the identification of the reaction byproducts which were also individually submitted to hydrotreatment under the same conditions.

2. Materials and methods

2.1. Catalyst preparation

The Pd catalyst was synthesized using Al-pillared clay (Al-PILC) as support. The starting clay was a purified-grade bentonite supplied by Fisher Scientific Company (Loughborough, Oregon, USA) with a cation-exchange capacity (CEC) of 97 meq/100 g. The Al-PILC was prepared following the procedure described elsewhere [31]. Pd was incorporated by wet impregnation of Al-PILC using solutions of PdCl₂ in HCl 0.1 M. The resulting wet solid was dried at room temperature for 2 h, at 110 °C for 14 h and finally calcined for 2 h at 500 °C. The catalyst, with a nominal 1 wt% load, is referred as Pd-PILC.

2.2. Catalyst characterization

A Micromeritics Tristar 3000 apparatus was used to obtain the N₂ adsorption-desorption isotherms at 77 K. The samples were previously outgassed at 160 °C and 5 × 10⁻³ Torr for 16 h. The specific surface area was obtained from the BET method. The Pd content was measured by inductively coupled plasma mass spectroscopy (ICP-MS) by means of a Model Elan 6000 Sciex Perkin-Elmer apparatus.

The particle size distribution of the metallic phase was determined by transmission electron microscopy (TEM) using a JEOL 2100F microscope with a point resolution of 0.19 nm coupled with an energy-dispersive X-ray spectrometer (EDXS; INCAx-sight, Oxford Instruments) used for elemental analysis.

A Micromeritics ChemiSorb 2705 pulse analyzer was used to determine the Pd dispersion of the catalysts by CO chemisorption at 25 °C. The chemisorption stoichiometry used was Pd/CO 1:1. The sample (0.1 g) was first cleaned with helium and then reduced at 90 °C for 2 h under hydrogen flow (20 NmL/min). Then, it was cooled under helium flow up to 25 °C and several pulses of CO were then introduced until saturation of the catalyst surface was achieved.

2.3. HDC and HDN experiments

The HDC/HDN experiments were performed in a thermostated stirred glass batch reactor (1.1 L total capacity) at 25 ± 0.5 °C and 1 atm using continuous H₂ flow at 50 ± 0.1 NmL/min (mass flow

controller Brooks Instruments mod. 0154, flow meters Smart Mass Flow 5860S, Brooks Instruments). The catalyst load was always 1 g/L and the starting concentration of the target compound was 100 mg/L in all cases. Experiments were performed using 4-chloronitrobenzene (4-CNB) (SIGMA, 99%), 4-chloroaniline (4-CA) (FLUKA 97%), aniline (PANREAC, >99%) and nitrobenzene (NB) (SIGMA, 99%). Magnetic stirring was used at 360 ± 0.1 rpm. All the catalysts were dried overnight at 120 °C before reduction. Then reduction was performed in a fixed-bed reactor (Pyrex glass, 30 cm length, 9 mm internal diameter) under continuous 35 NmL/min H₂ flow at 90 °C during 2 h [7]. After reduction, N₂ was passed at 35 NmL/min for 30 min.

The reduced catalyst was loaded into the batch glass reactor and 1 L of an aqueous solution of 100 mg/L of the starting compound was added to the corresponding amount of catalyst ([catalyst]₀ = 1 g/L). The stirring was maintained during 15 min before starting the H₂ feed. Samples were withdrawn from the reactor at 5, 10, 15, 30 min and each hour until the end of the experiment. The catalyst was separated by filtration using 0.45 µm pore size PTFE filters. Internal and external diffusion limitations were discarded in our working conditions after some preliminary experiments where the effect of stirring velocity and particle size was checked. Stirring velocities within 300–600 rpm were tested and no differences in 4-CNB conversion were found. A stirring velocity of 360 rpm was used in all the following batch experiments. The catalyst was used in powder with a particle size lower than 100 µm so that internal diffusion limitations are unlikely.

The stability of the catalyst was checked upon long-term (100 h) continuous experiments carried out in a fixed-bed reactor (Pyrex glass, 30 cm length, 9 mm internal diameter). The catalyst (0.1 g) with particle size < 100 µm was mixed with 2 mm glass beads and surrounded by glass wool in order to avoid channeling. Aqueous solutions of 4-CNB and aniline (100 mg/L) were fed at 0.42 mL/min (space-time ≈ 6.3 and 3.7 kg_{catal}/mol, respectively) and H₂ was continuously passed at 1 NmL/min. Liquid samples were periodically taken from the reactor exit upon the time on stream.

The Turnover Frequency (TOF) values have been calculated by:

$$\text{TOF}(\text{s}^{-1}) = \frac{r_0 \times M_A \times 10^{-3}}{D \times 60} \times 100 \quad (1)$$

where r_0 represents the initial reaction rate (mmol min⁻¹ g⁻¹_{metal}), M_A the atomic mass of Pd (g/mol) and D the metal dispersion (%).

Selectivity to cyclohexanone (S_{ketone}) from either 4-CA or aniline was calculated by the following expression:

$$S_{\text{ketone}}(\%) = \frac{[\text{Ketone}]_t}{[C_{i0} - C_{it}]} \times 100 \quad (2)$$

2.4. Analytical methods

Aniline, phenol and 4-CA were analyzed by HPLC with UV detector at 210 nm wavelength. A C18 column was used as stationary phase and acetonitrile-water or methanol-water (1:1, v/v, flow 1 mL/min) as mobile phase. Cyclohexanone, 4-CNB and NB were analyzed by means of a GC/FID using a CP-Wax 52 CB Varian capillary column (30 m length and 0.25 mm i.d.). In order to obtain information on the condensation byproducts, samples were analyzed by GC/MS with an electron impact ionization source (Saturn 2100 T). The column used was a Factor Four Varian (30 m length, 0.25 mm i.d.). The NIST05 library was used for the assessment of the species detected. Chloride concentration was quantified by means of anionic suppression Ionic Chromatography (Metrohm, mod. 761 Compact IC) with a conductivity detector using a Supp 5 column (25 cm length, 4 mm diameter) and a mixture of 1 mM NaHCO₃ and 3.2 mM Na₂CO₃ aqueous solution as mobile phase. Ammonium was measured using a specific electrode (Orion) connected to a Thermo

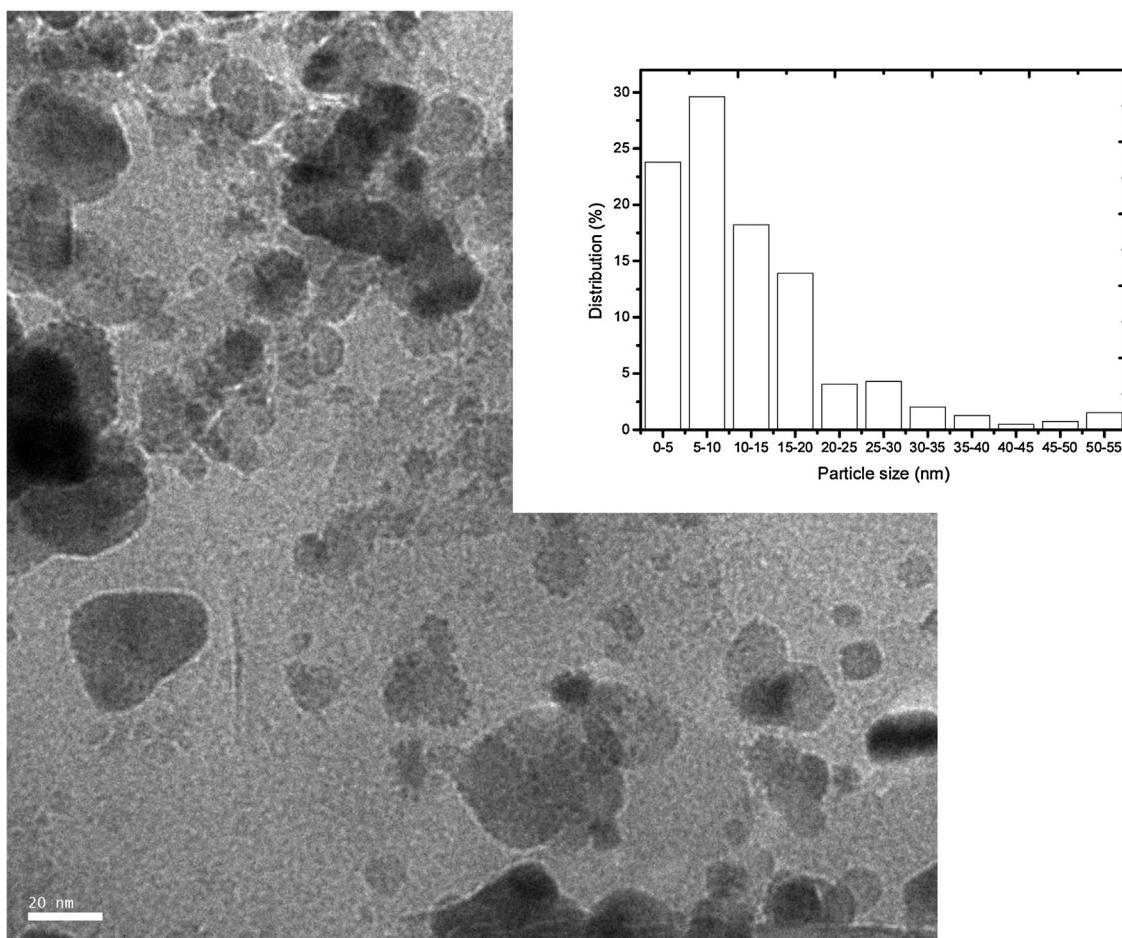


Fig. 1. TEM images and particle size distribution of Pd-PILC catalyst.

Scientific Orion High Performance detector. To allow complete conversion of ammonium into ammonia a 10 M NaOH solution was added to each sample in a 10% (v/v) dilution. The raw data reproducibility calculated from triplicate tests using the same catalyst was better than $\pm 5\%$. The repeatability of the analyses was $\pm 1\%$ in the case of HPLC and ionic chromatography and $\pm 3\%$ for GC/FID.

3. Results and discussion

3.1. Catalyst characterization

A BET surface area of $172 \text{ m}^2/\text{g}$ was measured for the catalyst, lower than that of the Al-PILC support ($212 \text{ m}^2/\text{g}$).

The Pd dispersion obtained from CO chemisorption was 8.3%. Fig. 1 shows a TEM micrograph of the catalyst. A wide size distribution of Pd nanoparticles, from less than 4 nm to more than 20 nm was observed, being the mean particle size around 5–10 nm (inner graph in Fig. 1).

3.2. HDC/HDN of 4-CNB

The reaction of 4-CNB with H_2 is a complex process where different byproducts are formed. In order to get a better understanding of this process, the hydrotreatment of the main byproducts, such as NB, 4-CA and aniline, has been individually investigated to complete the HDC/HDN pathway of 4-CNB.

Fig. 2 shows the results obtained from the HDC/HDN of 4-CNB with the Pd-PILC catalyst at 25°C and 1 atm. As can be seen, 4-CNB was quite rapidly converted under those ambient-like operating

conditions. Complete dechlorination was achieved in about 1 h. At that time all the chlorine removed from the 4-CNB molecule was analyzed as chloride ion, thus confirming that no other chlorinated species were remaining. Different chlorinated byproducts were detected although not quantified by GC/MS at low reaction time (up to 15 min), as summarized in Table 1.

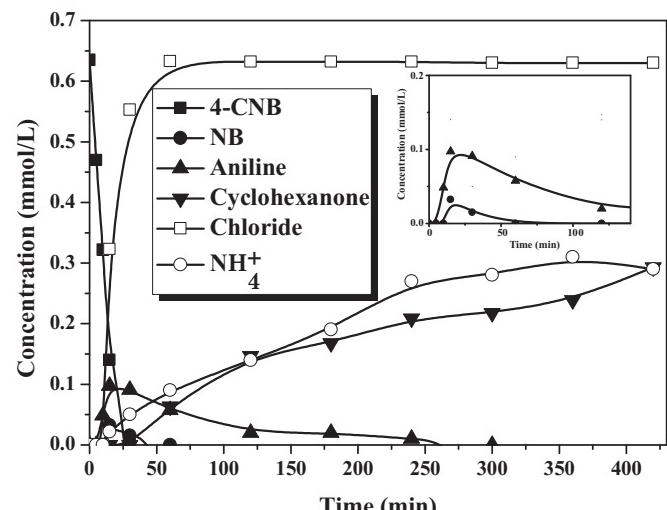


Fig. 2. HDC/HDN of 4-CNB with Pd-PILC (25°C , 1 atm, pH_0 6, $[\text{catalyst}]_0 = 1 \text{ g/L}$, $[4\text{-CNB}]_0 = 0.63 \text{ mmol/L}$ (100 mg/L), $Q\text{H}_2 = 50 \text{ NmL/min}$).

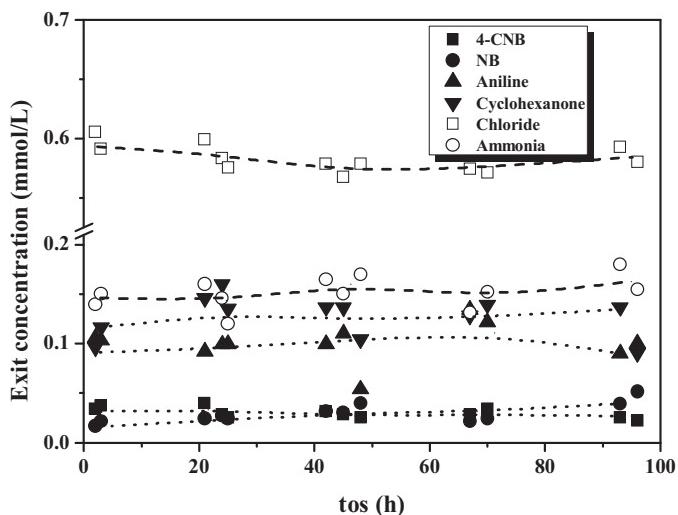


Fig. 3. Long-term experiment of 4-CNBr HDC/HDN with the Pd-PILC catalyst (25°C , 1 atm, pH_0 3, space-time: $6.3 \text{ kg}_{\text{cat}} \text{ h/mol}$, $[4\text{-CNBr}]_0 = 0.63 \text{ mmol/L}$, $\text{QH}_2 = 1 \text{ NmL/min}$).

Table 1

GC/MS identified byproducts from HDC of 4-CNBr with the Pd-PILC catalyst within the first 15 min of reaction.

| GC Retention time (min) | Compound |
|-------------------------|-------------------------------------|
| 3.39 | Aniline |
| 5.05 | <i>p</i> -Chloroaniline |
| 5.36 | 1-Chloro-4-nitrobenzene |
| 8.93 | <i>p</i> -Chloro-cis-azobenzene |
| 9.97 | Bis-(4-chloro-phenyl)-diazene |
| 10.03 | <i>p</i> -Chloroazobenzene (isomer) |
| 11 | <i>p,p'</i> -Dichloroazoxybenzene |

The main intermediate products obtained from this process were 4-CA (very low concentration not shown in Fig. 2), NB (also at very low concentration) and aniline while cyclohexanone was the main final product identified and quantified after 7 h of

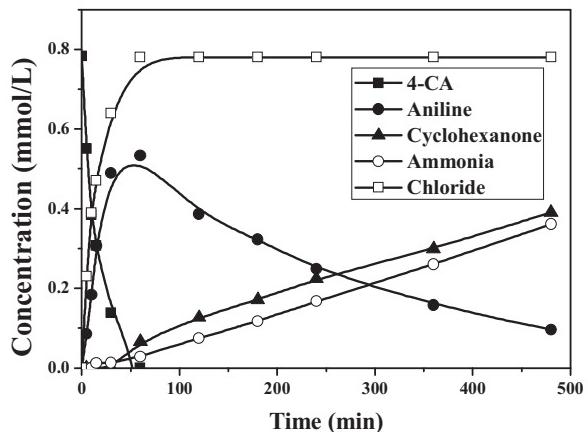


Fig. 4. HDC/HDN of 4-CA with Pd-PILC (25°C , 1 atm, pH_0 6, $[\text{catalyst}]_0 = 1 \text{ g/L}$, $[4\text{-CA}]_0 = 0.78 \text{ mmol/L}$ (100 mg/L), $\text{QH}_2 = 50 \text{ NmL/min}$).

reaction time, reaching near 47% of the stoichiometric amount corresponding to the initial concentration of 4-CNBr. The two intermediate products, NB and aniline, disappeared completely after 1 and 5 h of reaction time, respectively (Fig. 2). N-phenylcyclohexylamine (dimmer produced in the HDN of aniline, as it will be later described) and azobenzene were detected by GC/MS but not quantified. The production of ammonium follows the same trend observed for cyclohexanone.

It is important to remark that in previous works related to the HDC of 4-CNBr in aqueous phase no other chlorinated intermediates than 4-CA were detected using Pd-Fe, Ni-Fe, Ru and Fe-Pd nanoparticles as catalysts [8–11]. Those works were dealing with selective hydrodechlorination into aniline and further HDN was not considered.

To learn on the stability of the catalyst, a long-term (100 h) continuous experiment of 4-CNBr HDC/HDN was carried out as detailed in the experimental section. This experiment was carried out at pH_0 3, which favors this process as it will be later discussed. The results are shown in Fig. 3 where it can be seen that the Pd-PILC catalyst maintained a frankly stable performance upon the 100 h on

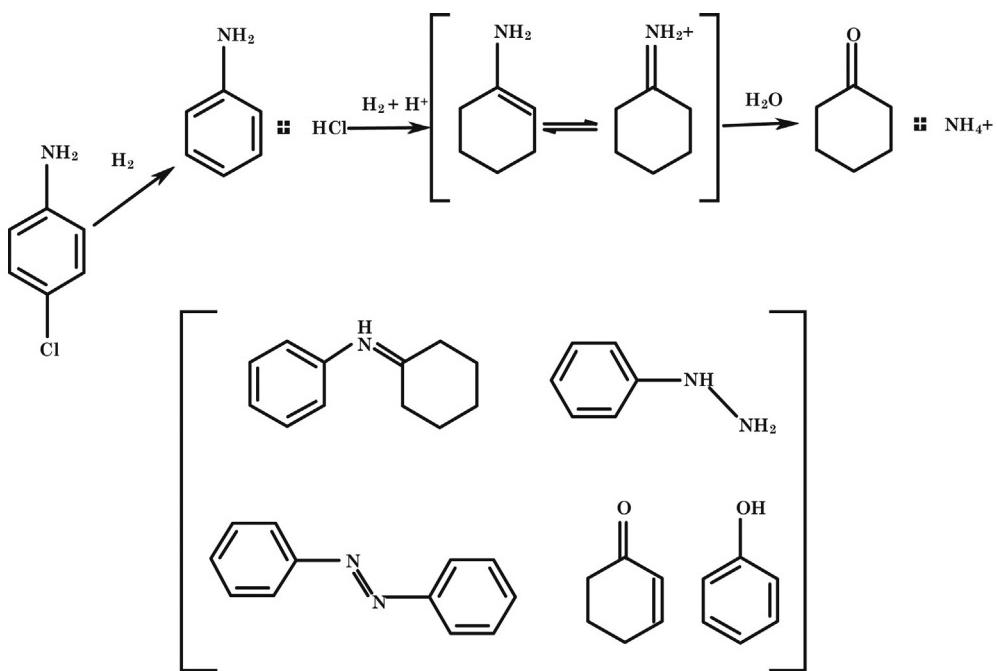


Fig. 5. Reaction scheme for HDC/HDN of 4-CA in aqueous phase with the Pd-PILC catalyst.

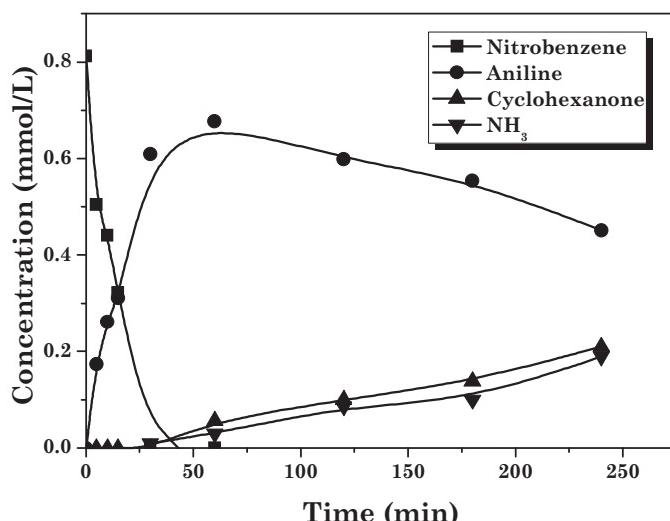


Fig. 6. HDN of nitrobenzene with Pd-PILC (25 °C, pH₀ 6, 1 atm, [catalyst]₀ = 1 g/L, [NB]₀ = 0.81 mmol/L (100 mg/L), QH₂ = 50 NmL/min).

stream. The conversion of 4-CNB and the distribution of reaction byproducts remained fairly constant as well as the pH of the exit stream (4.1–4.2), which was higher than that of the feed (3) because of the formation of NH₃ (see Fig. 2).

3.3. HDC/HDN of 4-CA

Dechlorination of 4-CA proceeds quite rapidly as can be seen in Fig. 4. It was completed in around 1 h and at that time all the chlorine was as chloride ion. The resulting aniline evolves to cyclohexanone and ammonia following the trend observed in Fig. 2 thus confirming that the formation of cyclohexanone upon HDC/HDN of 4-CNB results from further hydrogenation and hydrolysis of primarily formed aniline. This involves enamine/imine nucleophilic substitution [24].

The amount of cyclohexanone quantified, near to 0.4 mmol/L, at the end of the experiment (8 h) represents around one-half the corresponding stoichiometric from the initial concentration of 4-CA, ammonium being produced in almost the same amount (Fig. 4). Cyclohexenone and N-phenylcyclohexylamine were also detected but not quantified in the final effluent by GC/MS in addition to azobenzene and phenylhydrazine. From these results the reaction scheme of Fig. 5 is proposed.

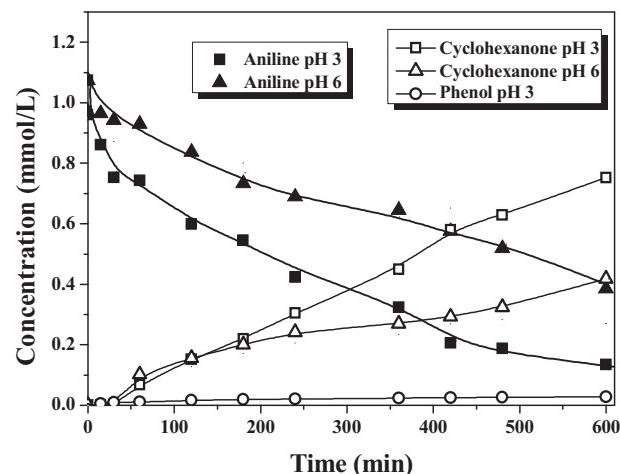


Fig. 7. HDN of aniline with Pd-PILC at different pH₀ (25 °C, 1 atm, [catalyst]₀ = 1 g/L, [Aniline]₀ = 1.07 mmol/L (100 mg/L), QH₂ = 50 NmL/min).

HDC of 4-CA to aniline in aqueous phase with Ru/TiO₂ catalyst has been studied by Vaidya and Dussa (2012) [13]. Aniline was converted to cyclohexylamine due to the selectivity of the catalyst towards hydrogenation of the aromatic ring rather than HDN.

3.4. HDN of nitrobenzene

Aniline was the primary and main product from HDN of NB with the Pd-PILC catalyst under ambient-like conditions, as can be seen in Fig. 6. That reaction proceeds quite rapidly and then aniline evolves at slower rate to cyclohexanone and ammonia.

Several reaction routes have been proposed for the hydrogenation of nitrobenzene in aqueous phase, with Pd/Fe(OH)_x [32] or Ni/TiO₂ catalysts [33]. In those routes azobenzenes and aniline are reported as the main reaction products. The condensation route to azobenzenes and the direct conversion into aniline have been described in other solvent media [34–36].

3.5. HDN of aniline

Direct hydrogenation of aniline in aqueous phase with the Pd-PILC catalyst confirmed the results of Figs. 4 and 6 but a significant increase of the reaction rate and the final conversion of aniline into cyclohexanone was achieved by lowering the initial pH, as can be

Table 2

Values of the kinetic constants, initial rate, TOF and selectivity to cyclohexanone for the hydrotreatments tested.

| | Reaction conditions | k (L min ⁻¹ g _{metal} ⁻¹) | r ² | r ₀ (mmol min ⁻¹ g _{metal} ⁻¹) | TOF × 10 ² (s ⁻¹) | Selectivity to cyclohexanone (%) |
|-----------------------|--------------------------|---|----------------|---|--|----------------------------------|
| Aniline hydrogenation | pH ₀ 6 25 °C | 0.44 ± 7.5 × 10 ⁻³ | 0.99 | 0.48 ± 1.3 × 10 ⁻² | 1.0 ± 7.6 × 10 ⁻² | 62 (4 h) 61 (10 h) |
| | pH ₀ 6 35 °C | 0.98 ± 5.4 × 10 ⁻² | 0.99 | 1.05 ± 6.9 × 10 ⁻² | 2.2 ± 0.2 | n.d. |
| | pH ₀ 6 50 °C | 1.44 ± 7.8 × 10 ⁻² | 0.97 | 1.55 ± 9.9 × 10 ⁻² | 3.3 ± 0.4 | n.d. |
| | pH ₀ 3 25 °C | 0.81 ± 4.8 × 10 ⁻² | 0.99 | 0.87 ± 6.0 × 10 ⁻² | 1.8 ± 0.2 | 48 (4 h) 80 (10 h) |
| | pH ₀ 10 25 °C | 0.20 ± 2.4 × 10 ⁻³ | 0.99 | 0.21 ± 4.7 × 10 ⁻³ | 0.4 ± 3.2 × 10 ⁻² | 57 (4 h) 41 (10 h) |
| HDC of 4-CA | pH ₀ 6 25 °C | 10.0 ± 0.38 | 0.98 | 7.85 ± 0.38 | 17.0 ± 1.6 | 50 (8 h) |
| | pH ₀ 6 35 °C | 11.0 ± 0.43 | 0.97 | 8.58 ± 0.42 | 18.0 ± 1.8 | n.d. |
| | pH ₀ 6 50 °C | 19.0 ± 0.29 | 0.99 | 14.8 ± 0.38 | 31.0 ± 2.3 | n.d. |
| NB hydrogenation | pH ₀ 6 25 °C | 6.15 ± 2.3 × 10 ⁻² | 0.99 | 4.98 ± 6.9 × 10 ⁻² | 10.6 ± 0.7 | 20 (4 h) |
| | pH ₀ 6 35 °C | 12.5 ± 0.63 | 0.99 | 10.1 ± 0.61 | 21.6 ± 2.3 | n.d. |
| | pH ₀ 6 50 °C | 23.7 ± 0.28 | 0.99 | 19.2 ± 0.42 | 41.1 ± 2.9 | n.d. |
| HDC of 4-CNB | pH ₀ 6 25 °C | 7.37 ± 0.39 | 0.99 | 4.64 ± 0.29 | 9.9 ± 1.1 | 47 (7 h) |
| | pH ₀ 6 35 °C | 11.9 ± 0.15 | 0.99 | 7.52 ± 0.17 | 16.1 ± 1.1 | n.d. |
| | pH ₀ 6 50 °C | 22.9 ± 0.91 | 0.99 | 14.4 ± 0.72 | 30.8 ± 3.0 | n.d. |

n.d.: not determined.

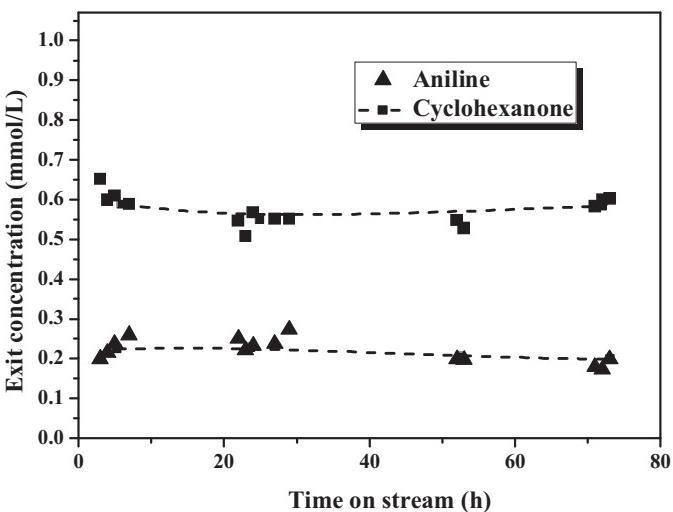


Fig. 8. Long-term experiment of aniline HDN with Pd-PILC (25 °C, pH₀ 3, space-time: 3.7 kg_{cat} h/mol, [Aniline]₀ = 1.07 mmol/L, QH₂ = 1 NmL/min).

seen in Fig. 7. At pH₀ 3 more than 90% of aniline was converted after 10 h reaction time, with 80% selectivity to cyclohexanone (Table 2). Whereas at pH₀ 6 that selectivity remained almost constant (\approx 62%) with time it increased monotonically at pH 3. Increasing the initial pH up to 10 a decrease of the selectivity to cyclohexanone was observed upon reaction time.

| Time on stream (h) | Conversion (E) |
|--------------------|----------------|
| 0 | 0.085 |
| 20 | 0.085 |
| 40 | 0.085 |
| 60 | 0.085 |
| 80 | 0.085 |

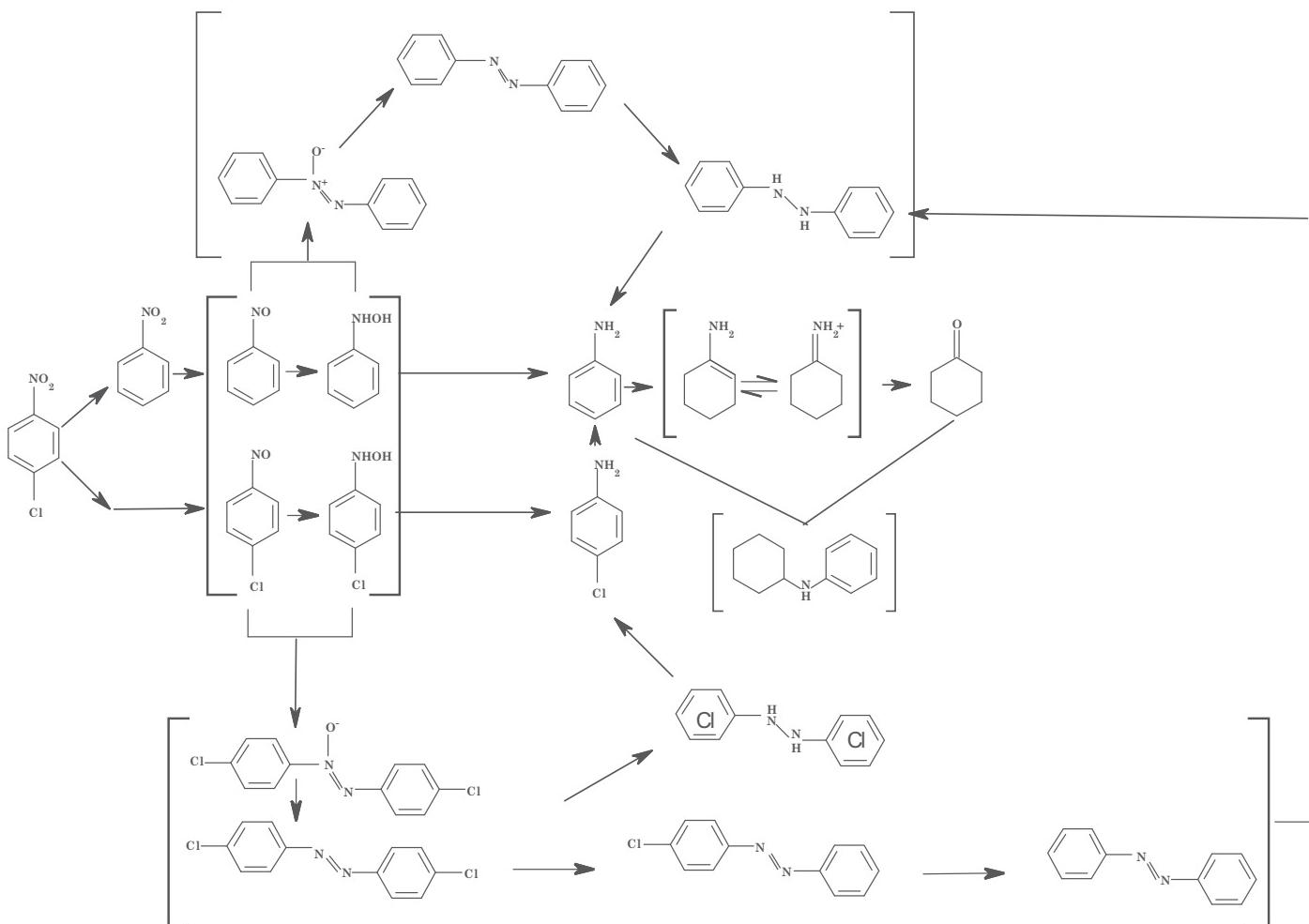


Fig. 9. Reaction scheme of 4-CNBD/HDC/HDN in aqueous phase with Pd-PILC.

3.6. Reaction pathway for HDC/HDN of 4-CNB

From the results so far, the reaction scheme of Fig. 9 is proposed for 4-CNB HDC/HDN in aqueous phase with the Pd-PILC catalyst at ambient conditions. 4-CNB can be initially dechlorinated to nitrobenzene or produce chlorinated intermediates which evolve to 4-CA. Aniline results from HDC of 4-CA or from nitrobenzene hydrogenation. Hydrogenation of nitrobenzene to aniline proceeds through the formation of nitrosobenzene and phenylhydroxylamine. Then aniline is converted by nucleophilic substitution with water molecules into cyclohexanone which can react with more aniline to yield N-phenylcyclohexylamine. The species detected by GC/MS at different reaction times prove that condensation of some chlorinated intermediates may also take place in the early stages. According to the literature, condensation of chloronitrosobenzene with chlorophenylhydroxylamine species produces chloroazobenzenes [41]. Besides, nitrosobenzene can also react with phenylhydroxylamine to form azobenzenes [36].

3.7. Kinetic analysis

The concentration-time curves describing the disappearance of each of the starting compounds tested in the different HDC/HDN experiments were fitted to pseudo-first order rate equations. A nonlinear regression program with the Marquardt algorithm at the 95% probability level was used. Table 2 summarizes the values obtained for the kinetic constants at different temperatures and initial pH values (in the case of aniline), as well as the corresponding disappearance initial rate and TOF values. These values confirm that dechlorination is a much easier process than denitration. HDC of 4-CNB proceeds at somewhat slower rate than that of 4-CA possibly due to the electron donor transfer effect of the amino group versus the acceptor character of the nitro. Nevertheless the differences disappear as the temperature increases. The values of k , r_0 and TOF corresponding to the experiments with aniline increased significantly as the initial pH decreased (see values at 25 °C) confirming two aforementioned higher activity of the catalyst at acidic pH.

From the Arrhenius equation were obtained values of activation energy for the disappearance of 4-CNB, 4-CA, NB and aniline. These values were 36 ± 0.3 ; 21 ± 6 ; 43 ± 5 and 37 ± 11 kJ/mol, respectively. Sokolskii et al. (1986) [42] reported an activation energy value of 50 ± 5 kJ/mol for hydrogenation of aniline with a Rh catalyst within 50–90 °C.

4. Conclusions

Catalytic hydrogenation with Pd (1 wt%) supported on pillared clay has proved to be a promising solution for the abatement of chloronitrogenated pollutants in water under ambient-like conditions. Complete dechlorination of 4-CNB has been achieved followed by further conversion into cyclohexanone as the main reaction product. Experiments with the reaction intermediates allowed learning on the reaction pathway. Nitrobenzene and 4-chloroaniline were identified as primary products, which evolve to aniline in relatively short time, which is finally converted into cyclohexanone as the main product of this reaction being favored at acidic pH. N-phenylcyclohexylamine was also identified in much lower amount, resulting from reaction of cyclohexanone with aniline. GC/MS analyses allowed identifying different chlorinated intermediates within the early stages of the process (up to 15 min) but complete dechlorination was achieved in about 1.5 h.

The catalyst showed a frankly good stability upon 100 h on stream. An initial TOF value close to 0.1 s^{-1} was obtained for

4-CNB disappearance at 25 °C and 36 ± 0.3 kJ/mol for the activation energy.

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